

CHAPTER 1.7 - Guidance for Discharges with Water Quality Additives

This chapter is designed to help calculate use restrictions and determine WET monitoring frequencies when additives are used. This guidance is intended to apply to discharges that contain biocides or other additives and are made up of noncontact cooling water, contact cooling water, boiler blowdown, or cooling tower blowdown.

NOTICE: This document is intended solely as guidance, and does not contain any mandatory requirements except where requirements found in statute or administrative rule are referenced. This guidance does not establish or affect legal rights or obligations, and is not finally determinative of any of the issues addressed. This guidance does not create any rights enforceable by any party in litigation with the State of Wisconsin or the Department of Natural Resources. Any regulatory decisions made by the Department of Natural Resources in any matter addressed by this guidance will be made by applying the governing statutes and administrative rules to the relevant facts.

What is an “Additive”?

For purposes of this discussion, any chemical compound intentionally added to the wastestream is hereafter referred to as an “additive”. The term “additive” includes biocides used for anti-fouling, surfactant-based detergents, anti-scaling compounds, and other chemicals used in noncontact cooling water, contact cooling water, boiler blowdown, and/or cooling tower blowdown waters. (NOTE: Section NR 106.10, Wis. Adm. Code, exempts chlorine in non-contact cooling waters if it is not “intentionally” introduced into the discharge – i.e. present due to the water supply).

Research into the toxicity of additives has shown great potential for toxicity to aquatic life by many of these compounds. Biocides are specifically designed to kill biological organisms and are usually of greatest concern. As with other chemical-specific compounds, the more additives present, the greater the potential for toxicity due to additive or synergistic effects. Guidance related to assessing the need for use restrictions and/or WET monitoring to prevent effluent toxicity due to these compounds is given below.

Is the Following Guidance Appropriate or Should the WET Checklist Be Used to Determine WET Monitoring Frequencies?

The WET Checklist (described in Chapter 1.3) was designed to help Department staff make decisions regarding WET limits and monitoring frequencies for surface water discharges, based on their potential to exhibit toxicity. The Checklist assesses a discharge’s toxicity potential by asking questions relating to industry type (or industrial contributions, if municipal), treatment efficiency and operations, the presence of individual compounds measured in the wastewater, and other factors. Since many of these factors are usually absent in situations where the discharge does not contain process wastewaters (i.e., discharges made up solely of noncontact cooling water, contact cooling water, boiler blowdown, and/or cooling tower blowdown), the WET Checklist does not apply very well to many of those situations. However, since these discharges may have the potential to exhibit toxicity or exceed water quality standards, especially if water quality additives are present, another thought process is needed to determine whether it is necessary to limit the use of additives and/or use WET to control the discharge of potentially toxic effluents.

This chapter is intended to deal with situations that do not fit well into the Checklist, specifically those situations where use restrictions for additives and/or WET monitoring may be needed to control toxicity in discharges made up of noncontact cooling water, contact cooling water, boiler blowdown, and/or cooling tower blowdown. To clarify when this chapter should be used in the place of the WET Checklist, these discharges have been divided into two categories:

Case 1: Discharges made up of noncontact cooling water, contact cooling water, boiler blowdown, or cooling tower blowdown are Case 1 if any substance listed in ch. NR 105, Wis. Adm. Code, Tables 1-9, or Chapter 1.3,

Additional Compounds of Concern ARE detected in the effluent. In most cases, the WET Checklist is appropriate and should be used to determine the need for WET limits and monitoring for Case 1 dischargers.

Case 2: Discharges made up of noncontact cooling water, contact cooling water, boiler blowdown, or cooling tower blowdown are Case 2 if any substance listed in ch. NR 105, Wis. Adm. Code, Tables 1-9, or Chapter 1.3, *Additional Compounds of Concern* ARE NOT detected in the effluent. The procedure contained in this chapter should be used to determine the need for use restrictions and WET monitoring frequency for Case 2 dischargers.

NOTE: If a discharge is solely noncontact cooling water, contact cooling water, boiler blowdown, and/or cooling tower blowdown and no additives are used, then it is not necessary to complete the process described below or the WET Checklist - use restrictions and/or WET monitoring are usually not needed in those situations.

Information Needed for Calculating Use Restrictions

When reviewing a Case 2 discharger, the first step is to determine the stream flow (usually the $Q_{7,10}$) to effluent flow (Q_e) ratio. Depending on that ratio, the following steps should be taken:

Step 1A: If the $Q_{7,10}:Q_e$ ratio $> 1,000:1$, no effluent limitations or WET tests are recommended, but the following language is recommended in the permit or briefing memo as deemed necessary by the permit drafter:

"Effluent limits and WET monitoring are not recommended for water quality additives in Outfall ____ because the $Q_{7,10}:Q_e$ ratio $> 1,000:1$. It is recommended that label instructions be followed for ____ [Additive Name(s)]. It is further recommended that the Department be notified of any changes in the use of water quality additives consistent with the requirements of s. NR 205.07(3), Wis. Adm. Code."

Step 1B: If the $Q_{7,10}:Q_e$ ratio $\leq 1,000:1$, go to Step 2 to determine if effluent limitations or WET monitoring is needed.

Step 2A: Required Information For WDNR Review. When an application indicates that an additive may be discharged, the information listed in (a) - (h) below is needed for each additive in order to determine if an effluent limitation or use restriction is warranted. If this information is available, proceed to Step 3A.

- a. Manufacturer of the additive.
- b. Chemical name of the additive.
- c. Active Ingredient(s) (if not proprietary information).
- d. CAS #(s) of the additive and/or active ingredients.
- e. Material Safety Data Sheet (MSDS) and/or official toxicity test results listing available aquatic life toxicity data for the WHOLE PRODUCT. Toxicity data for active ingredients is not acceptable for use in calculating a use restriction. The following types of data are acceptable:

Species	Endpoint of Concern
<i>Ceriodaphnia dubia</i> (Cladoceran)	48-hour LC_{50} or EC_{50}/IC_{25}
<i>Daphnia magna</i> (Cladoceran)	48-hour LC_{50} or EC_{50}/IC_{25}
<i>Lepomis macrochirus</i> (Bluegill Sunfish)	96-hour LC_{50} or EC_{50}/IC_{25}
<i>Pimephales promelas</i> (Fathead Minnow)	96-hour LC_{50} or EC_{50}/IC_{25}
<i>Oncorhynchus mykiss</i> (Rainbow Trout)	96-hour LC_{50} or EC_{50}/IC_{25}

LC_{50} = the estimated concentration of additive that would cause 50% mortality to the test population following the given time period

EC_{50} = the estimated concentration of additive that would cause a given effect in 50% of the test population following a given time period

IC_{25} = the estimated concentration of additive that would cause a 25% reduction in some biological measurement of

the test population following a given time period

NOTE: To calculate a use restriction it is necessary to have data from at least one of the cladoceran species and at least one of the fish species (according to s. NR 106.10(1), Wis. Adm. Code).

- f. Complete listing of toxicity test conditions. For an example, see Tables 11-14 in Weber (1993).
- g. Standardized test methodology (name of a specific method & its reference may be listed for this, such as “Acute Toxicity Test Procedures for *Daphnia magna*” in Weber (1993).) If a modification to a standardized method was used, provide the reference of the specific method along with a specific listing of and reasons for the modifications.
- h. Any noted observations from the toxicity tests.

Reference:

Weber, C. 1993. *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms*, 4th Ed. Environmental Monitoring Systems Laboratory, USEPA, Cincinnati, OH. EPA/600/4-90/027F.

Toxicity test results on water quality additives should be submitted to the Water Quality Standards Section, WDNR, 101 South Webster Street, P.O. Box 7921, Madison, WI 53707-7921.

Step 2B: If the information described in Step 2A is not available at the time of application, the permittee should be contacted with a request to provide the appropriate information prior to permit reissuance. Attachment 1 at the end of this chapter contains a summary of the needed information and can be shared with the permittee to help insure that the right information is made available. If this information is not available during the WQBEL determination process, proceed directly to Step 5B.

Calculating Numerical Use Restrictions

Step 3: For each additive with available aquatic life toxicity data, an effluent limitation should be calculated according to the following procedure:

- a. If at least one 48-h LC₅₀ or EC₅₀ value is available for *Ceriodaphnia dubia* or *Daphnia magna* and at least one 96-h LC₅₀ or EC₅₀ value is available for either fathead minnow, bluegill sunfish, or rainbow trout, the mean* LC₅₀ or EC₅₀ for each of these species shall be divided by 5 if rainbow trout are represented in the database or divided by 10 if rainbow trout are not represented in the database (according to s. NR 106.10, Wis. Adm. Code).

* = A geometric mean should be used when ≥ 3 data points are available for any single species.

- b. The resulting limitation shall be equal to the lowest resultant value calculated according to the procedures in (a).

TABLE 1.7.B EXAMPLE NUMERIC LIMITATION FOR ADDITIVES

Species	Duration	Concentration	Geometric Mean
Fathead Minnow	96-LC ₅₀	0.29 mg/L	0.54 mg/L
Fathead Minnow	96-LC ₅₀	0.72 mg/L	
Fathead Minnow	96-LC ₅₀	0.75 mg/L	
Rainbow Trout	96-LC ₅₀	1.34 mg/L	NA

<i>Daphnia magna</i>	48-LC ₅₀	0.13 mg/L	NA
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Lowest LC₅₀ = 0.13 mg/L for *Daphnia magna*. This value is divided by 5 since rainbow trout toxicity data are available. The limitation is equal to 0.026 mg/L as a daily maximum effluent concentration.

- c. A limitation can be calculated for an additive only if data are available for one cladoceran (*Ceriodaphnia dubia* or *Daphnia magna*) and at least one of the fish species listed in Step 2A(c) (according to s. NR 106.10, Wis. Adm. Code).

Determining Compliance with Numerical Limitations in WPDES Permits

An effluent limitation calculated as described above should be included in a WPDES permit as a daily maximum concentration limitation for the **WHOLE PRODUCT**. Reporting requirements and compliance determinations are as follows:

Step 4A: LIQUID FORMULATION - When determining compliance with effluent limitations for an additive dispensed as a **LIQUID**, the following additional reporting requirements should be included in the WPDES permit:

- a. Method of addition (i.e., slug vs. continuous vs. triggered, etc.).
- b. Amount of additive used per day (i.e., gallons, fluid ounces).
- c. Volume of treated effluent discharged per day (Q_e as gal/d).

End-of-pipe effluent concentrations should be reported as mg/L and should be calculated according to the following equation:

$$\text{Conc. (mg/L)} = \frac{(\text{Amount Added (fluid oz/day)} \times \text{Density (lbs/gal)} \times 0.0078125 \text{ gal/fluid oz} \times 453592 \text{ mg/lb})}{(3.785 \text{ liters/gal} \times Q_e \text{ gal/d})}$$

Step 4B: SOLID FORMULATION - When determining compliance with effluent limitations for an additive dispensed as a **SOLID**, the following additional reporting requirements should be included in the WPDES permit:

- a. Method of addition (i.e., slug vs. continuous vs. triggered, etc.).
- b. Amount of additive used per day (i.e., ounces).
- c. Volume of treated effluent discharged per day (Q_e as gal/d).

End-of-pipe effluent concentrations should be reported as parts per million (ppm) and should be calculated according to the following equation:

$$\text{Conc. (ppm)} = \frac{\text{Amount Added (oz/day)}}{Q_e \text{ (MGD)} \times 16 \text{ oz/lb} \times 8.34 \text{ lbs/gal}}$$

Determining the Need for Whole Effluent Toxicity (WET) Testing

Step 5A: Any Case 2 discharger who uses additives may opt to conduct WET tests in lieu of having end-of-pipe limitations placed in a permit. The permittee should notify the WDNR in writing prior to or during the public-notice period that this is the preferred method of compliance.

Step 5B: WET tests should be utilized to determine the potential for impacts to the receiving stream fish and aquatic life community under any of the following discharge conditions:

- a. When additive toxicity data required in Step 2A are not made available to the WDNR.
- b. When historical or projected use of an additive suggests that the dosage necessary to be effective in production or treatment exceeds 1/5 of the daily maximum limitation calculated as suggested above.
- c. Whenever a discharge contains two or more additives that may be discharged simultaneously.

Step 5C: The need for acute and/or chronic WET monitoring should be decided based on the following dilution scenarios:

If $Q_{7,10}:Q_e > 1000:1$, no WET testing is recommended, since dilution is high and the potential for impacts due to toxicity are lower. Department staff may, in certain circumstances, determine that testing is necessary despite high dilution, but this decision should be clearly documented in the permit file, so others can tell why decisions were made.

If $Q_{7,10}:Q_e \leq 1000:1$ & $> 100:1$, only acute testing is recommended, since dilution is high and the potential for impacts due to chronic toxicity are lower. Staff may, in some instances, determine that chronic testing is necessary despite high dilution, but this decision should be clearly documented in the permit file, so others can tell why decisions were made.

If $Q_{7,10}:Q_e \leq 100:1$, both acute and chronic WET testing is recommended.

Frequency of WET Testing

Step 6: The frequency of WET testing discussed in this section represents the **minimum** recommended to evaluate the reasonable potential for additive-related impacts to the receiving stream fish and aquatic life community. These recommended frequencies may be increased if there are case-specific reasons that warrant a further evaluation of the reasonable potential.

- a. When an additive is discharged independently and isn't likely to be mixed with other additives, a discharger should be required to conduct a WET test on effluent that is likely to contain that additive or its residual at least once per year for the first two years following permit issuance. This recommendation applies independently to each additive used unless otherwise noted.
- b. When two or more additives are used such that there is a chance that they are discharged simultaneously, a discharger should be required to conduct a WET test on effluent that is likely to contain that mixture or the residual of the mix at least once per year for the first two years following permit issuance.
- c. When > 2 additives are used and there is little chance that they are discharged simultaneously, a discharger should be required to conduct a WET test on the effluent at least once every three months for the first eighteen months following permit issuance. Effluent samples should be collected at a time when it is likely that an additive or its residual may be present in the effluent.
- d. Best professional judgement should be used to determine if any unusual circumstances exist that may warrant additional testing. Examples of discharge/additive-specific circumstances that may require additional testing include: known effects of temperature on the toxicity of an additive, changes in the receiving stream species composition on a seasonal basis, etc.

When To Require WET Limits

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WET limits are required according to ch. NR 106, Wis. Adm. Code., whenever “...*the RPF calculated according to par. (b) exceeds 0.3. Whole effluent toxicity limits may be imposed, on a case-by-case basis, whenever facility-specific whole effluent toxicity test data indicate toxicity to aquatic life as determined in s. NR 106.09. Whole effluent toxicity limits may also be imposed in the absence of facility-specific whole effluent toxicity test data, on a case by-case-basis, whenever facility-specific or site-specific data or conditions indicate toxicity to aquatic life that is attributable to the discharger.*”

Noncontact cooling water, contact cooling water, boiler blowdown, and/or cooling tower blowdown discharges are subject to the same reasonable potential determinations and should be given WET limitations when available data suggests they are necessary. Staff should evaluate these discharges using the same logical process as that described in Chapter 1.3 to determine whether WET limits are necessary. Although the WET Checklist may not apply directly to these discharges, staff should use other guidance in Chapter 1.3 and their best professional judgement to determine which data is representative of the discharge and appropriate for use in calculating the reasonable potential factor (RPF). If the $RPF \geq 0.3$, a WET limit is required, according to s. NR 106.08, Wis. Adm. Code, and should be placed in the permit along with a compliance schedule and WET monitoring (usually quarterly monitoring after the limit has become effective). If the discharge is located in the Great Lakes Basin, then the *WET reasonable potential (RP) procedures in Great Lakes Basin* discussion in Chapter 1.3 (page 28) should also be considered.

ATTACHMENT 1

Information Needed For WDNR Review of Water Quality Additives

Whenever an additive is used, the following information listed in (a) - (h) below should be submitted for each additive, in order for the WDNR to determine if an effluent limitation or use restriction is warranted at the time of permit (re)issuance.

- a. Manufacturer of the additive.
- b. Chemical name of the additive.
- c. Active Ingredient(s) (if not proprietary information).
- d. CAS #(s) of the additive and/or active ingredients.
- e. Material Safety Data Sheet (MSDS) and/or official toxicity test results listing available aquatic life toxicity data for the WHOLE PRODUCT. Toxicity data for active ingredients is not acceptable for use in calculating a use restriction. The following types of data are acceptable:

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<i>Pimephales promelas</i> (Fathead Minnow)	96-hour LC ₅₀ or EC ₅₀ /IC ₂₅
<i>Oncorhynchus mykiss</i> (Rainbow Trout)	96-hour LC ₅₀ or EC ₅₀ /IC ₂₅

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IC₂₅ = the estimated concentration of additive that would cause a 25% reduction in some biological measurement of the test population following a given time period

NOTE: To calculate a use restriction it is necessary to have data from at least one of the cladoceran species and at least one of the fish species (according to s. NR 106.10(1), Wis. Adm. Code).

- f. Complete list of toxicity test conditions. Examples to follow include Tables 11 – 14 in Weber (1993).
- g. Standardized test methodology (name of a specific method & its reference may be listed for this, such as “Acute Toxicity Test Procedures for *Daphnia magna*” in Weber (1993). If a modification to a standardized method was used, provide the reference of the specific method along with a specific listing of and reasons for the modifications).
- h. Any noted observations from the toxicity tests.

Toxicity test information on water quality additives should be submitted to the Water Quality Standards Section, WDNR, 101 South Webster Street, P.O. Box 7921, Madison, WI 53707-7921.

Reference:

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Cincinnati, OH. EPA/600/4-90/027F.